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(54) Title: NOVEL SURFACTANT COMPOSITIONS AND THE USE THEREOF IN PAPER DEINKING

(57) Abstract

Mixtures of C_8 to C_{22} alpha-olefin sulfonates and alkyl ether sulfates of the formula: $RO-(CH_2CH_2O)_{1-4}SO_3Na$ where R is C_8-C_{18} alkyl, with one or more of alkoxylates of C_1-C_{10} alcohols, dialkoxylates of certain cyclohexenyl diacids, or propoxylated quaternary ammonium compounds; and mixtures of fatty acid alkoxylates, fatty alcohol alkoxylates, and one or more of said cyclohexenyl diacid dialkoxalates and C_1-C_{10} alcohol alkoxylates, provide enhanced removal of ink when used in the froth flotation deinking of waste paper.

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NOVEL SURFACTANT COMPOSITIONS AND THE USE THEREOF IN PAPER DEINKING

The present invention relates to the treatment of waste paper to remove ink from the paper. More specifically, the present invention relates to novel surfactant compositions useful in the removal of ink from waste paper, and to the use of such novel surfactant compositions in the removal of ink from the paper.

The growing interest in recycling of used ("waste") paper as a source in the manufacture of new paper and paper products has increased the demand for effective products and processes which are adaptable to the processing of the many different types of paper currently used in commerce. In particular, there remains a strong interest in processes and reagents which are useful in the removal of ink from the waste paper. Obviously, it is highly desirable to maximize removal of ink from waste paper to permit the recycled waste paper to be as bright and clean as possible. Ideally, such reagents should be able to maximize removal of ink from types of paper currently known in commerce including newsprint, impact printed paper and non-impact printed paper. Such differing types of paper and the differing types of ink that may be used thereon, pose a challenge in the identification of useful, efficient surfactant formulations and processes which can be used in the removal of the ink from the paper. This challenge is particularly seen when the waste paper feedstock comprises a mixture of types of paper, as is

often the case when the paper is obtained from business and industrial concerns.

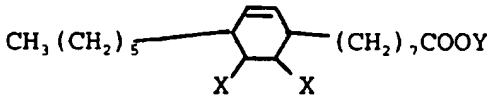
The prior art demonstrates that various surfactants and surfactant combinations have been employed in the deinking of paper. While the techniques disclosed in the prior art may have been useful, nonetheless they are less than ideal for various reasons. Thus, there remains a need for surfactant formulations which exhibit the effectiveness and efficiency exhibited by the compositions in the present invention.

For instance, U.S. Patent No. 4,311,552 discloses deinking waste material, such as waste newsprint, in a slurrying process using a deinking agent which comprises a C_{14} to C_{20} alpha olefin sulfonate, particularly in combination with a nonionic detergent such as a 9-mole phenyl ethoxylate.

U.S. Patent No. 4,935,096 discloses deinking of waste paper, using as the deinking agent an ionic surfactant, alone or in combination with nonionic surfactants. Among the disclosed ionic surfactants, are anionic compounds derived from alkylbenzene or hydrocarbons, such as sodium alkylbenzene sulfonates, sodium alcohol ether sulfates, sodium alcohol sulfates, and sodium alkyl or dialkyl sulfosuccinates. Among the disclosed cationic surfactants are mono, di or tri alkyl quaternary ammonium compounds. Among the nonionic surfactants disclosed are alkyl phenyl ethoxylates, ethoxylates of alcohols or fatty acids, and "mixed ethylene/propylene oxide adducts".

U.S. Patent No. 4,964,949 discloses deinking of waste paper employing a deinking agent which comprises a reaction product of one or more alkylene oxides with natural oils or fats and polyhydric alcohols, and also comprises a compound selected from the group consisting of alkylene oxide adducts of C_{12} to C_{18} alcohols, or sulfates of alkylene oxide adducts of C_{12} to C_{18} alcohols, or C_8 to C_{22} fatty acids or salts thereof.

U.S. Patent No. 5,158,697 discloses deinking of waste paper wherein the deinking agent comprises one or more of alkoxylated dimer acids and polymer acids of unsaturated fatty acids containing 16 to 20 carbon atoms; alkoxylates of partial esters of dimer acids and polymer acids of unsaturated fatty acids containing 16 to 20 carbon atoms esterified with alcohol containing 1 to 18 carbon atoms; or alkoxylated dicarboxylic acids or dicarboxylic acid monoesters of the following formula



wherein one of the X groups is COOH and the other is H or CH_3, Y is H or R, and R is an alkyl group containing 1 to 18 carbon atoms.

The present invention is directed to a deinking composition useful in the froth flotation deinking of waste paper, comprising a surfactant mixture selected from the group consisting of

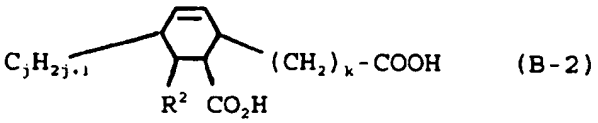
(A) mixtures of

(A.1) an anionic surfactant component selected from the group consisting of alpha-olefin sulfonates containing 8 to 22 carbon atoms, alkyl ether sulfates of the formula $R^1O-(CH_2CH_2O)_nSO_3Na$ wherein n is 1 to 4, R^1 is C_8-C_{18} alkyl, and mixtures thereof; and

(A.2) a second surfactant component selected from the group consisting of

(A.2.a) alkoxylates of straight and branched C_1-C_{10} alcohols wherein the alkoxylate moiety contains propoxy and ethoxy units in a propoxy:ethoxy mole ratio of 0.5:1 to 2.0:1;

(A.2.b) dialkoxylates of diacids of the formula (B-2)



(B-2)

wherein R^2 is H or CH_3, j is 1-11, k is 1-11 and (j + k) is 10-14, the dialkoxylate containing a total of up to 60 propoxy and ethoxy units in a propoxy:ethoxy mole ratio of 0.2:1 to 4.0:1; and

(A.2.c) propoxylated quaternary ammonium compounds of the formula $(R^3)_3-N-CH_2CH_2O(PrO)_{9-40}-H\bullet A^-$ wherein PrO denotes propoxy, each R^3 is independently a C_1-C_{12} alkyl group, and A is a halide, acetate, phosphate, methylsulfate or ethylsulfate anion; and

(B) mixtures of

(B.1) a mixture of one or more fatty acid alkoxylates wherein the fatty acyl moiety contains 12 to 18 carbon atoms and the alkoxylate portion contains 10-

30 ethoxy units and 5-25 propoxy units, one or more alkoxylates of C_{12}-C_{20} alcohols with 10-30 ethoxy units and 5-25 propoxy units; and

(B.2) a third surfactant component selected from the group consisting of

(B.2.a) alkoxylates of diacids as defined in (A.2.b) and

(B.2.b.) alkoxylates of straight and branched C_1-C_{10} alcohols as defined in (A.2.a).

The present invention is also directed to a process of deinking waste paper, by subjecting the waste paper to froth flotation in a liquid composition comprising a surfactant mixture selected from the group consisting of

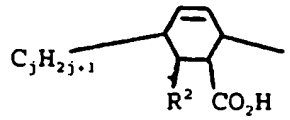
(A) mixtures of

(A.1) an anionic surfactant component selected from the group consisting of alpha-olefin sulfonates containing 8 to 22 carbon atoms, alkyl ether sulfates of the formula R^1O-$(CH_2CH_2O)_nSO_3Na$ wherein R is C_8-C_{18} alkyl and n is 1 to 4, and mixtures thereof; and

(A.2) a second surfactant component selected from the group consisting of

(A.2.a) alkoxylates of straight and branched C_1-C_{10} alcohols wherein the alkoxylate moiety contains propoxy and ethoxy units in a propoxy:ethoxy mole ratio of 0.5:1 to 2.0:1;

(A.2.b) dialkoxylates of diacids of the formula (B-2)



wherein the R^2 group is CH_3 or H, j is 1-11, k is 1-11 and (j + k) is 10-14, the dialkoxylate containing a total of up to 60 propoxy and ethoxy units in a propoxy:ethoxy mole ratio of 0.2:1 to 4.0:1; and

(A.2.c) propoxylated quaternary ammonium compounds of the formula $(R^3)_3$-N-CH_2CH_2O-$(PrO)_{9-40}$-H●A wherein PrO denotes propoxy, each R is independently a C_1-C_{12} alkyl group, and A is a halide, acetate, phosphate, methylsulfate or ethylsulfate anion; and

(B) mixtures of (B.1) a mixture of one or more fatty acid alkoxylates wherein the alkoxylate portion contains 10-30 ethoxy units and 5-25 propoxy units, one or more alkoxylates of C_{12}-C_{20} alcohols with 10-30 ethoxy units and 5-25 propoxy units; and

(B.2) a third surfactant component selected from the group consisting of

(B.2.a) alkoxylates of diacids as defined in (A.2.b) and

(B.2.b.) alkoxylates of straight and branched C_1-C_{10} alcohols as defined in (A.2.a).

In a particularly preferred aspect, waste paper is slurried and subjected to froth flotation in a liquid medium comprising any of the foregoing mixtures of surfactants, whereby ink and the waste paper are separated in the liquid medium, and then separating the slurried waste paper from the liquid medium containing the solubilized ink.

The compositions of the present invention are particularly useful in removal of ink from waste paper and more particularly from waste paper comprising mixtures comprising two or more distinct types of paper, whether the paper has been imprinted by conventional impact-printing techniques with any of the inks used in that type of printing, or by non-impact printing techniques (such as laser printing) using any of the types of inks used in that kind of printing.

One component present in many of the compositions of the present invention is an anionic surfactant component which is an alpha-olefin sulfonate, alkyl ether sulfate, or a mixture thereof. By alpha-olefin sulfonates are meant sulfonates of straight and branched alkenyl groups containing 8 to 22 carbon atoms and containing at least one carbon-carbon double bond, as well as the hydroxylated counterparts thereof, including but not limited to compounds exhibiting either of the following formulas (A.1.a) and (A.1.b), or mixtures thereof,

$$R^a\text{-}CH{=}CHSO_3Na \qquad (A.1.a)$$

$$R^a\text{-}CHOH\text{-}CH_2SO_3Na \qquad (A.1.b)$$

wherein R^a is a straight or branched alkyl group, preferably straight, selected so that the molecule as a whole contains 8 to 20 carbon atoms. Preferred examples of these anionic surfactants include alpha-olefin sulfonates containing 14 to 16 carbon atoms in the molecule.

By alkyl ether sulfate is meant compounds of the formula (A.1.c)

$$R^1O-(CH_2CH_2O)_nSO_3Na \quad (A.1.c)$$

wherein n is 1 to 4, and R is C_8-C_{18} alkyl.

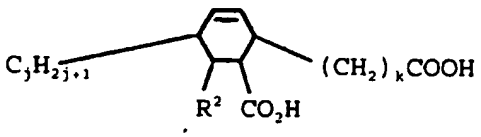
Anionic surfactants of the foregoing formulas are commercially available and can readily be synthesized using known industrial chemical techniques. Preferred commercial examples include "Witconate AOS", a C_{14}-C_{16} alpha-olefin sulfonate, and "Witcolate ES-3", a sodium lauryl ether sulfate corresponding to the foregoing formula (A.1.c) wherein n is 3 and R^1 is C_{12}-C_{14} alkyl, both of which are sold by Witco Corp.

The foregoing anionic surfactants have been found to be particularly effective and efficient in the removal of ink from waste paper, particularly when used in froth flotation processes as described below, when the anionic surfactant component is used in combination with any of several second surfactant components, namely the following.

One such second surfactant component comprises one or more alkoxylates of straight and/or branched alcohols, which alcohols contain 1 to 10 carbon atoms. The alcohols are alkoxylated with both propoxy and ethoxy units, such that the resulting alkoxylate has a mole ratio of propoxy units to ethoxy units of 0.5:1 to 2.0:1. In this and all other alkoxylated compounds described herein, the ethoxy and propoxy units can be present as poly(ethoxy) and poly(propoxy) blocks, or can

be intermingled. It will be understood that useful alcohol alkoxylates include any of this formula which can form the desired surfactant composition of the present invention exhibiting the desired properties described herein. Thus, the range of molecular weights, or chain lengths, of alcohol alkoxylates of the foregoing description which are useful in the compositions of the present invention vary rather widely. An alcohol alkoxylate of the foregoing description will be effective depending on the other components of the composition, but for illustrative purposes it should be understood that the molecular weight of useful alcohol alkoxylates of the foregoing description may generally range from about 1000 to about 10,000, without intending to be bound by the precise numerical values. Satisfactory alkoxylated alcohols meeting the foregoing descriptions can be readily synthesized using established industrial synthesis techniques, although numerous examples of satisfactory alkoxylated alcohols are commercially available. One exemplary commercially available alkoxylated alcohol is "Witconol NS-500LQ", a high molecular weight alkoxylated butanol.

Another class of alkoxylates useful in combination with the anionic surfactants described hereinabove, are dialkoxylates of diacids of the formula (B-2)



(B-2)

wherein R^2 can be H or CH_3, wherein the diacid is dialkoxylated, that is, substituted at both -COOH sites with alkoxylate chains containing propoxy and ethoxy units in a propoxy:ethoxy mole ratio of 0.2:1 to 2.0:1. The propoxy and ethoxy units can be interspersed or can be present as blocks formed from each type of unit. The number of moles of alkoxy units in the dialkoxylated diacid can fall within the range of chain lengths which still enable the alkoxylated diacid to function effectively in the surfactant composition as described herein. For purposes of illustration, however, satisfactory dialkoxylated diacids will generally contain up to 75 alkoxy units, and preferably 20 to 60 alkoxy units in total. The compounds can have a molecular weight in the range of about 1200 to about 3000.

Alkoxylated diacids of this description can be readily formed by reacting the corresponding diacid, which is commercially available, with an appropriately chosen number of moles of ethylene oxide and propylene oxide under conventional alkoxylating conditions. Satisfactory diacids include "Westvaco Diacid 1550" and "Westvaco Diacid 1575", available from the Westvaco Corp. in which the principal diacid component corresponds to formula (B-2) wherein the substituent R^2 is H. These diacids are disclosed more generally in U.S. Patent No. 3,899,476.

As is shown in the example herein, effective deinking of paper feedstock has also been obtained using as the surfactant component (even as the sole surfactant

component) one or more dialkoxylates of cyclohexenyl diacid derivatives of the foregoing formula (B-2).

Another type of surfactant which has been found to exhibit exemplary results when used in deinking operations in combination with the anionic surfactant component described herein, is propoxylated quaternary ammonium compounds of the formula (A.2.c)

$$(R^3)_3\text{-}N\text{-}CH_2CH_2O(PrO)_{9\text{-}40}\text{-}H\bullet A^- \qquad (A.2.c)$$

wherein (PrO) denotes the propoxy unit, each of the R^3 groups is independently C_1-C_{12} alkyl and A is a halide, acetate, phosphate, methyl sulfate, or ethyl sulfate anion. Preferably, one of the R^3 groups is methyl and two R^3 groups are ethyl. More preferably, A represents chloride.

Propoxylated quaternary ammonium compounds of the foregoing formula (A.2.c) can readily be synthesized, and several examples are commercially available. More specifically, compounds known as "Emcol CC-9" and "Emcol CC-42", which are propoxylated methyl diethyl quaternary ammonium compounds of the foregoing formula containing, respectively, 9 and 40 propoxy units, are commercially available from Witco Corp. Since these compounds are cationic, the ability of these propoxylated quaternary ammonium compounds to form together with the foregoing anionic surfactants a surfactant composition useful in the deinking of waste paper is particularly surprising in that it is conventionally expected that cationic and anionic

substances would interact with each other (because of their opposing ionic charges) rather than cooperating synergistically to function as effectively as they have been found to function.

The anionic surfactant component on the one hand, and the second surfactant component on the other hand which as defined hereinabove can be alcohol alkoxylate, dialkoxylate of cyclohexenyl diacids, or propoxylated quaternary ammonium compounds, are present together in amounts relative to each other effective to aid in the removal of ink from the waste paper. Generally, the weight ratio of the anionic surfactant or surfactants to the second surfactant (i.e. the nonionic and/or cationic surfactant or surfactants) present should be from 20:1 to 1:20. More preferably, the weight ratio of the anionic surfactant component to the second surfactant component is about 5:1 to 1:1, and more preferably about 4:1 to about 1.5:1.

Additionally, surfactant compositions useful in accordance with the present invention comprise mixtures of fatty acid alkoxylate, a fatty alcohol alkoxylate, and a third surfactant component. The fatty acids represent one or a blend of fatty acids containing 12 to 18 carbon atoms. In the fatty acid alkoxylates, the alkoxylate portion contains 10-30 ethoxy units and 5-25 propoxy units. The fatty alcohol alkoxylate is preferably derived from fatty alcohols containing 16 to 20 carbon atoms, and is substituted with an alkoxylate chain containing propoxy and ethoxy units in a propoxy:ethoxy mole ratio of 0.5:1 to 2.0:1.

Typically, without intending to be bound hereby, the fatty alcohol alkoxylate should exhibit a molecular weight in the range of about 1000 to about 3000.

It has been determined that a mixture of the fatty acid alkoxylate and fatty alcohol alkoxylate with a third surfactant exhibits exemplary results in the deinking of waste paper, especially when the third surfactant is an alkoxylate of a cyclohexenyl diacid as defined hereinabove with respect to alkoxylates of diacids of the formula (B-2), and when the third surfactant is an alkoxylate of straight or branched C_1-C_{10} alcohol as described hereinabove.

In those surfactant compositions of the present invention comprising one or more fatty acid alkoxylates, fatty alcohol alkoxylate, and the indicated third surfactant component such as dialkoxylates of cyclohexenyl diacids or alkoxylates of alcohols, the weight ratio of the fatty acid alkoxylate to the fatty alcohol alkoxylate is from 1:1 to 10:1, and the ratio of the fatty acid alkoxylate plus fatty alcohol alkoxylate to the third surfactant component is from 1:20 to 20:1, but is preferably in the range of 5:1 to 1:1 and more preferably about 2:1 to 1:1.

The surfactant formulations of the present invention can be produced by simply combining the indicated surfactant components in the desired relative amounts, such as by stirring in a suitable tank until the components are thoroughly and homogeneously intermixed. Water may be present, in an amount ranging

from 0.1 wt.% to 90 wt.% depending on the desired final concentration of active ingredients.

In general, effective deinking is provided by intimately contacting the waste paper with any of the surfactant formulations of the present invention, preferably in an aqueous or other liquid medium to provide desired fluidity and penetration of the surfactant components to the paper/ink interface. Preferably, the waste paper is first shredded or otherwise converted to small pieces so as to improve the contact of the paper and ink with the liquid medium bearing the surfactants. Of course, appropriate agitation can be provided to enhance the desired contact between the surfactant components and the paper/ink interface.

It is preferred to utilize the surfactant compositions of the present invention in connection with the froth flotation of ink from the waste paper. The general conditions of froth flotation deinking techniques are known in this field. The waste paper is pulped in an aqueous bath, which has preferably been rendered alkaline by appropriate adjustment of the pH via the addition of a base such as sodium hydroxide. Preferably, the pH is about 9 to 11. The desired surfactants are added at amounts calculated to provide the desired ratio between amounts of the respective compounds. The overall amount of surfactant is selected with respect to the quantity of the paper in the cell and with respect to the general amount of ink product on the paper. Generally, the total amount of surfactant

comprises about 0.1 wt.% to about 5.0 wt.% and preferably up to about 1.0 wt.% based on the amount of waste paper present. Lesser amounts of surfactant risk reducing the efficiency of the deinking, whereas higher amounts of surfactant may assist in the deinking of waste paper but not necessarily enhance the efficiency of the deinking in proportion to the additional amounts of surfactant used. The flow of gas, typically air, through the flotation cell agitates the liquid medium and the waste paper, provides enhanced contact with the surfactant, and propels ink particles removed from the waste paper to the top surface where a froth rich in removed ink is established. The froth can be removed continuously or intermittently. After a period of time appropriate for the volume of the cell and the quantity of waste paper and its ink content, the pulp of deinked waste paper is removed from the cell for further processing toward the recovery and reuse in regenerated paper products.

The present invention has been found to provide improved effectiveness and efficiency in the deinking of waste paper, particularly waste paper comprising mixtures of different types of paper. The enhanced deinking has been determined through analysis for the gain in brightness of the recovered paper product and for the percentage of ink removed, (in total and as large particle removal), as well as for the percentage of fiber recovered in the regenerated product.

The following examples demonstrate the significant and favorable results that are obtained in the practice of the present invention.

EXAMPLES

The feed material to be deinked was repulped in a commercial pulping apparatus (Morden Slushmaker). The feed material comprised about 90 wt.% ledger paper and about 10% copier paper (i.e. that had been printed on by a conventional photocopying machine). In both cases the ink formulations present contained hydrocarbon resins used as binders for pigments. Each batch contained 4 pounds of paper (dry weight) which was combined with enough water to form a pulp which comprised about 6 wt.% paper. This pulp was maintained in this apparatus for thirty minutes at about 120°F at a pH of 10 to which it had been adjusted with sodium hydroxide.

Each repulped batch was then diluted with water to 0.8 wt.% consistency and the temperature was adjusted to 100°F, after which portions of the resulting pulp were transferred from the pulping tank into a conventional deinking flotation cell. Once the flotation cell was full and the flow of water through the cell was adjusted to 15 gallons per minute, each of the surfactant compositions described below were added in separate runs. All surfactant compositions used were diluted to 68.1 grams per liter and were added at either 0.3, 0.6 or 0.9 wt.% (based on total dry solids of

surfactants weight). The surfactants added were allowed to mix for five minutes in the cell prior to starting air flow through the cell. Then, air flow upwards through the cell was started and adjusted to 8 cubic feet per minute and the cell was operated for an additional 10 minutes.

Samples of each pulp batch were collected before and after flotation, and were analyzed for brightness and dirt count measurements. Six air dry filter pads were produced from the deinked paper, and were used for brightness measurements. Also, the "dirt count" (large ink particles remaining) was measured with an image analyzer at 25X magnification. In addition, the froth was collected and weighed, for yield calculations.

The various surfactant combinations tested are described in Tables 1-A and 1-B. The results of the testing are set forth in Table 2.

The results in Table 2 and Table 3-B demonstrate that the surfactant components of the present invention provide superior deinking of waste paper.

TABLE 1-A

Surfactant	Description
A	A dialkoxylate of "Westvaco Diacid 1575" with a total of 13.5 moles of ethylene oxide ("EO") and 7.5 moles of propylene oxide ("PO") per mole of diacid
B	A (60:40) (wt.)) mixture of fatty acid alkoxylate with a blend of alkoxylates of C_{16}-C_{20} alcohols (with 15 moles of EO and 7 moles of PO)
C	A dialkoxylate of "Westvaco Diacid 1575" with a total of 7.5 moles of EO and 7.5 moles of PO per mole of diacid
D	A dialkoxylate of "Westvaco Diacid 1575" with a total of 2.5 moles of EO and 7.5 moles of PO per mole of diacid
E	Sodium C_{14}-C_{16} olefin sulfonate ("Witconate AOS")
F	Polyoxypropylene (9) methyl diethyl ammonium chloride ("Emcol CC-9")
G	Polyoxypropylene (40) methyl diethyl ammonium chloride ("Emcol CC-42")
H	Butoxy alkoxylate with 60 moles of EO and 55 moles of PO ("Witconol NS-500 LQ")
I	Sodium laureth-3 sulfate
J	Lauryl dimethylamine oxide("Emcol LO")

TABLE 1-B

Surfactant(s) Mixture No.	Description
1	40 wt.% A 60 wt.% B
2	100 wt.% B
3	40 wt.% C 60 wt.% B
4	40 wt.% D 60 wt.% B
5	80 wt.% E 20 wt.% F
6	80 wt.% E 20 wt.% G
7	80 wt.% E 20 wt.% H
8	60 wt.% E 40 wt.% H
9	80 wt.% I 20 wt.% J
10	80 wt.% I 20 wt.% G

11		80 wt.% I 20 wt.% F
12		100 wt.% A
13*		100 wt.% L727 ("Lionsurf 727")
14*		100 wt.% "DI600"

*commercial products used as standards.

TABLE 2

Surfactant Mixture	% Active	Increase In Brightness	% Fiber Yield	% Ink Removal
1	0.3	4.1	98.2	75.9
	0.6	5.2	98.9	90.5
	0.9	4.3	99.4	79.3
2	0.3	5.6	97.8	87.2
	0.6	7.4	98.5	87.5
	0.9	6.8	99.1	87.5
3	0.3	8.7	96.5	88.1
	0.6	8.3	98.3	67.6
	0.9	9.2	98.8	81.2
4	0.3	4.4	98.3	49.6
	0.6	6.5	98.7	75.4
	0.9	4.7	99.4	85.4

5	0.3	4.0	98.5	86.5
	0.6	4.0	99.2	85.9
	0.9	3.4	99.6	75.9
6	0.3	4.3	98.4	89.4
	0.6	2.2	99.6	91.2
	0.9	2.1	99.7	91.7
7	0.3	4.1	98.4	90.4
	0.6	4.5	99.1	84.5
	0.9	2.9	99.6	86.4
8	0.3	3.7	98.5	93.9
	0.6	3.3	99.3	27.2
	0.9	2.7	99.6	81.1
9	0.3	3.6	98.6	90.0
	0.6	3.9	99.2	88.9
	0.9	2.6	99.7	82.3
10	0.3	2.9	98.8	92.8
	0.6	2.0	99.6	89.6
	0.9	1.7	99.8	93.0
11	0.3	3.2	98.6	85.0
	0.6	2.0	99.6	81.4
	0.9	0.3	100.0	82.3
12	0.3	4.5	98.2	81.3
	0.6	3.3	99.3	76.3
	0.9	3.1	99.6	76.5
13	0.3	5.2	97.9	90.0
	0.6	4.9	99.0	72.9
	0.9	3.7	99.5	92.7

1	14	0.3	3.0	98.8	91.8
		0.6	2.8	99.4	77.6
		0.9	2.8	99.6	82.5

In addition, the same procedure was carried out using as the surfactant various ethoxylated/propoxylated derivatives of the cyclohexenyl diacid "Westvaco Diacid 1575" defined hereinabove. The various alkoxylates are identified in Table 3-A, and the test results are set forth in Table 3-B.

TABLE 3-A

Surfactant	Alkoxylation (moles of EO/moles of PO)
K	13.5 EO/7.5 PO
L	25 EO/25 PO (block) (formulated)
M	25 EO/25 PO (random) (formulated)
N	25 EO/25 PO (random) (unformulated)
O	25 EO/7.5 PO (block) (formulated)
P	25 EO/7.5 PO (block) (neat)
Q	13.5 EO/7.5 PO (block) (formulated)
R	13.5 EO/7.5 PO (block) (neat)
S	"DI600" as standard
T	"Lionsurf 727" as standard

TABLE 3-B

Surfactant	% Active	Increase In Brightness	% Fiber Yield	% Ink Removal
L	0.3	3.8	85.6	91.5
	0.6	3.2	85.0	84.2
	0.9	3.2	86.2	60.7
M	0.3	3.4	93.2	95.0
	0.6	2.8	88.9	85.2
	0.9	2.9	88.6	77.7

1	N	0.3	3.5	92.5	92.7
		0.6	2.5	89.5	83.5
		0.9	2.7	87.2	80.2
	O	0.3	2.6	92.9	91.3
5		0.6	2.5	89.2	77.4
		0.9	1.5	88.8	15.9
	P	0.3	2.4	93.9	92.2
		0.6	1.8	90.1	56.7
		0.9	1.9	86.0	56.2
10					
	Q	0.3	0.9	97.8	73.3
		0.6	1.2	97.8	76.7
		0.9	0.9	98.0	44.3
	R	0.3	0.3	97.8	82.6
		0.6	0.9	97.0	67.0
15		0.9	1.3	98.2	44.9
	S	0.3	1.8	95.6	82.6
		0.6	1.6	96.9	79.8
		0.9	1.5	98.1	40.5
	T	0.3	1.7	96.2	91.8
20		0.6	1.3	96.3	75.1
		0.9	0.9	90.8	55.6

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WHAT IS CLAIMED IS

1. A deinking composition useful in the froth flotation deinking of waste paper, comprising a surfactant mixture selected from the group consisting of

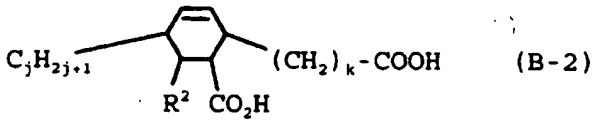
(A) mixtures of

(A.1) an anionic surfactant component selected from the group consisting of alpha-olefin sulfonates containing 8 to 22 carbon atoms, alkyl ether sulfates of the formula $R^1O-(CH_2CH_2O)_nSO_3Na$ wherein n is 1 to 4, and R^1 is alkyl containing 8 to 18 carbon atoms, and mixtures thereof; and

(A.2) a second surfactant component selected from the group consisting of

(A.2.a) alkoxylates of straight and branched C_1-C_{10} alcohols wherein the alkoxylate moiety contains propoxy and ethoxy units in a propoxy:ethoxy mole ratio of 0.5:1 to 2.0:1;

(A.2.b) dialkoxylates of diacids of the formula (B-2)



(B-2)

wherein R^2 is H or CH_3, j is 1-11, k is 1-11, and (j + k) is 10-14, the dialkoxylate containing a total of up to 60 propoxy and ethoxy units in a propoxy:ethoxy mole ratio of 0.2:1 to 4.0:1; and

(A.2.c) propoxylated quaternary ammonium compounds of the formula $(R^3)_3$-N-$CH_2CH_2O(PrO)_{9-40}$-H●A$^-$

wherein PrO denotes propoxy, each R^3 is independently C_1-C_{12} alkyl, and A is a halide, acetate, phosphate, methylsulfate or ethylsulfate anion; and

(B) mixtures of (B.1) a mixture of one or more fatty acid alkoxylates wherein the fatty acyl moiety contains 12 to 18 carbon atoms and the alkoxylate portion contains 10-30 ethoxy units and 5-25 propoxy units, one or more alkoxylates of C_{12}-C_{20} alcohols with 10-30 ethoxy and 5-25 propoxy units; and

(B.2) a third surfactant component selected from the group consisting of

(B.2.a) dialkoxylates of diacids as defined in (A.2.b) and

(B.2.b.) alkoxylates of straight and branched C_1-C_{10} alcohols as defined in (A.2.a).

2. A deinking composition according to Claim 1 comprising a surfactant mixture selected from the group consisting of mixtures of

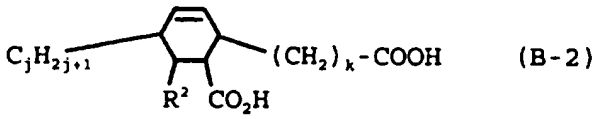
(A.1) an anionic surfactant component selected from the group consisting of alpha-olefin sulfonates containing 8 to 22 carbon atoms, alkyl ether sulfates of the formula R^1O-$(CH_2CH_2O)_nSO_3Na$ wherein n is 1 to 4, and R^1 is alkyl containing 8 to 18 carbon atoms, and mixtures thereof; and

(A.2) a second surfactant component selected from the group consisting of

(A.2.a) alkoxylates of straight and branched C_1-C_{10} alcohols wherein the alkoxylate moiety contains

propoxy and ethoxy units in a propoxy:ethoxy mole ratio of 0.5:1 to 2.0:1;

(A.2.b) dialkoxylates of diacids of the formula (B-2)



(B-2)

wherein R^2 is H or CH_3, j is 1-11, k is 1-11, and (j + k) is 10-14, the dialkoxylate containing a total of up to 60 propoxy and ethoxy units in a propoxy:ethoxy mole ratio of 0.2:1 to 4.0:1; and

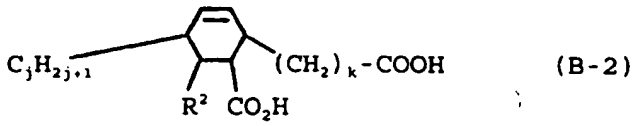
(A.2.c) propoxylated quaternary ammonium compounds of the formula $(R^3)_3$-N-$CH_2CH_2O(PrO)_{9-40}$-H●A$^-$ wherein PrO denotes propoxy, each R is independently C_1-C_{12} alkyl, and A is a halide, acetate, phosphate, methylsulfate or ethylsulfate anion.

3. A deinking composition according to Claim 2 comprising a surfactant mixture of (A.1) an alpha-olefin sulfonate containing 8 to 22 carbon atoms; and

(A.2.a.) an alkoxylate of straight or branched C_1-C_{10} alcohol wherein the alkoxyate moiety contains propoxy and ethoxy units in a propoxy:ethoxy mole ratio of 0.5:1 to 2.0:1.

4. A deinking composition according to Claim 2 comprising a surfactant mixture of (A.1) an alpha-olefin sulfonate containing 8 to 22 carbon atoms; and

(A.2.b.) a dialkoxylate of a diacid of the formula (B-2)



(B-2)

wherein R^2 is H or CH_3, j is 1-11, k is 1-11, and (j + k) is 10-14, the dialkoxylate containing a total of up to 60 propoxy and ethoxy units in a propoxy:ethoxy mole ratio of 0.2:1 to 4.0:1.

5. A deinking composition according to Claim 2 comprising a surfactant mixture of (A.1) an alpha-olefin sulfonate containing 8 to 22 carbon atoms; and

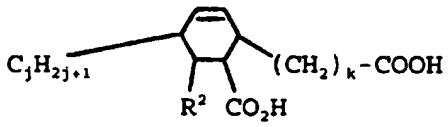
(A.2.c) a propoxylated quaternary ammonium compound of the formula $(R^3)_3$-N-$CH_2CH_2O(PrO)_{9-40}$-H●A^- wherein PrO denotes propoxy, each R is independently C_1-C_{12} alkyl, and A is a halide, acetate, phosphate, methylsulfate or ethylsulfate anion.

6. A deinking composition according to Claim 2 comprising a surfactant mixture of (A.1) an alkyl ether sulfate of the formula R^1O-$(CH_2CH_2O)_nSO_3Na$ wherein n is 1 to 4, and R^1 is alkyl containing 8 to 18 carbon atoms; and

(A.2.a) an alkoxylate of straight or branched C_1-C_{10} alcohol whereih the alkoxylate moiety contains propoxy and ethoxy units in a propoxy:ethoxy mole ratio of 0.5:1 to 2.0:1.

7. A deinking composition according to Claim 2 comprising a surfactant mixture of (A.1) an alkyl ether sulfate of the formula $R^1O-(CH_2CH_2O)_nSO_3Na$ wherein n is 1 to 4, and R^1 is alkyl containing 8 to 18 carbon atoms; and

(A.2.b) a dialkoxylate of a diacid of the formula (B-2)



(B-2)

wherein R^2 is H or CH_3, j is 1-11, k is 1-11, and (j + k) is 10-14, the dialkoxylate containing a total of up to 60 propoxy and ethoxy units in a propoxy:ethoxy mole ratio of 0.2:1 to 4.0:1.

8. A deinking composition according to Claim 2 comprising a surfactant mixture of (A.1) an alkyl ether sulfate of the formula $R^1O-(CH_2CH_2O)_nSO_3Na$ wherein n is 1 to 4, and R^1 is alkyl containing 8 to 18 carbon atoms; and

(A.2.c) a propoxylated quaternary ammonium compound of the formula $(R^3)_3-N-CH_2CH_2O(PrO)_{9-40}-H\bullet A^-$ wherein PrO denotes propoxy, each R is independently C_1-C_{12} alkyl, and A is a halide, acetate, phosphate, methylsulfate or ethylsulfate anion.

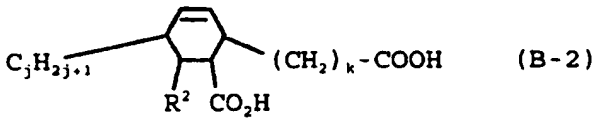
9. A deinking composition according to Claim 1 comprising a surfactant mixture selected from the group consisting of mixtures of

(B.1) a mixture of one or more fatty acid alkoxylates wherein the fatty acyl moiety contains 12 to 18 carbon atoms and the alkoxylate portion contains 10-30 ethoxy units and 5-25 propoxy units; one or more alkoxylates of C_{12}-C_{20} alcohols with 10-30 ethoxy and 5-25 propoxy units; and

(B.2) a third surfactant component selected from the group consisting of

(B.2.a) alkoxylates of straight and branched C_1-C_{10} alcohols wherein the alkoxylate moiety contains propoxy and ethoxy units in a propoxy:ethoxy mole ratio of 0.5:1 to 2.0:1; and

(B.2.b) dialkoxylates of diacids of the formula (B-2)



(B-2)

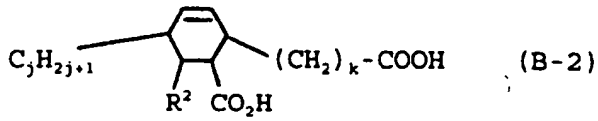
wherein R^2 is H or CH_3, j is 1-11, k is 1-11, and (j + k) is 10-14, the dialkoxylate containing a total of up to 60 propoxy and ethoxy units in a propoxy:ethoxy mole ratio of 0.2:1 to 4.0:1.

10. A deinking composition according to Claim 9 comprising

(B.2.a) an alkoxylate of straight or branched C_1-C_{10} alcohol wherein the alkoxylate moiety contains propoxy and ethoxy units in a propoxy:ethoxy mole ratio of 0.5:1 to 2.0:1.

11. A deinking composition according to Claim 9 comprising

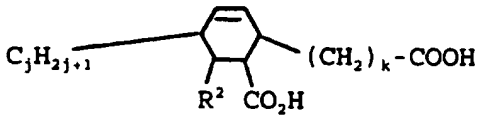
(B.2.b) a dialkoxylate of a diacid of the formula (B-2)



(B-2)

wherein R^2 is H or CH_3, j is 1-11, k is 1-11, and (j + k) is 10-14, the dialkoxylate containing a total of up to 60 propoxy and ethoxy units in a propoxy:ethoxy mole ratio of 0.2:1 to 4.0:1.

12. A deinking composition useful in the froth flotation deinking of waste paper, comprising one or more dialkoxylates of diacids of the formula (B-2)



(B-2)

wherein R^2 is H or CH_3, j is 1-11, k is 1-11, and (j + k) is 10-14, the dialkoxylate containing a total of up to 60 propoxy and ethoxy units in a propoxy: ethoxy mole ratio of 0.2:1 to 4.0:1.

13. The method of deinking waste paper comprising subjecting said waste paper to froth flotation in an aqueous medium comprising a composition in accordance with any of claims 1 to 12.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/16389

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :D21C 5/02
US CL :162/5; 510/174
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 162/5; 510/174

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,311,552 A (BRUCATO et al) 19 January 1982, see entire document.	1-12
Y	US 5,158,697 A (KAWAMORI et al) 27 October 1992, see entire document.	1-12
Y	US 4,964,949 A (HAMAGUCHI et al) 23 October 1990, see whole document.	1-12
A	US 4,935,096 A (GALLAGHER et al) 19 June 1990, column 2, line 6 through column 3, line 34.	1-12

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search	Date of mailing of the international search report
03 JANUARY 1997	0 3 FEB 1997
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/16389

B. FIELDS SEARCHED
Electronic data bases consulted (Name of data base and where practicable terms used):

APS, DIALOG, STN
search terms: deink?, alkyl ether sulfates, alkoxylate? alcohol?, dialkoxylate? diacids, propoxylated quaternary ammonium, fatty acid alkoxylate?